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The impact of reduction in the benzene limit value in gasoline on airborne benzene, toluene and xylenes levels

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Abstract

Background benzene, toluene, xylenes (BTX) average concentrations have been measured over the urban agglomeration of Toulouse, France, during both springtime and summer periods of 1999 and 2001.

The benzene average amount over the two Toulouse campaigns in 1999 is equal to $2.2 \mu\text{g}/\text{m}^3$, very close to the French air quality standard and well under the average value of $5 \mu\text{g}/\text{m}^3$ recommended by European Economic Community countries, recognising that those regulations are given for a whole year. BTX pollution over Toulouse has, in particular, been produced by motor vehicle exhaust gases.

For the study conducted during the same periods of 2001, benzene concentrations were within the French quality value in the whole area. This is because the benzene limit value contained in gasoline went from 5% to 1 % since 2000 January 1.

It will be important to measure benzene over annual periods in order to know its exact values over such a period and to observe its potential seasonal variations.

Keywords: Benzene; Toluene; Xylene; Passive dosimeter; Urban area; BTX; Volatile organic compound (VOC)

1. Introduction

Volatile organic compounds (VOCs) play an important role in atmospheric chemistry. This is especially true for substituted aromatic VOC such as toluene and xylenes which have a high photochemical ozone creation potential. They take part in photochemical reactions and are major sources of radicals

which can oxidise NO to NO₂, the precursor of ozone (Finlayson-Pitts and Pitts, 2000; Reis et al., 2000). Exposure to benzene has the potential for adverse health effects as it is a genotoxic carcinogen (Snyder and Kalf, 1994; Zhang et al., 1996; Lovern et al., 1997).

The regulation of major indicators for atmospheric pollution (ozone, nitrogen dioxide and sulphur dioxide) has been updated in recent years to include additional compounds like benzene. The ORAMIP, in partnership with the "Chemistry Energy and Environment" laboratory of the ENSIA-CET, has undertaken a background benzene, to-

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luene, xylene (BTX) average concentration measurement over the urban agglomeration of Toulouse during both springtime and summer periods of 1999 (May 5th to May 26th and June 14th to July 2nd) and 2001 (May 2nd to May 22nd and June 13th to July 4th).

The objective of our work was to evaluate *BTX average background concentrations* over a period of several weeks and to compare the BTX concentrations between 1999 and 2001. Samplers of passive type were selected for that purpose and were proved accurate tools under our experimental conditions. Due to their low cost and the simplicity of their positioning, it was possible to multiply the number of measurement points and hence to obtain a more precise pollution map of the area.

2. Methodology

2.1. BTX sampling and analysis

BTX sampling can be carried out by various methods using Tedlar or Teflon bags, canisters or adsorbents, respectively. The latter allow a sampling in either dynamic or passive mode. The advantage of a passive sampling mode is to provide a direct estimate of the average pollutant concentration corresponding to an acquisition period varying between few hours and few days (Brown, 1993; Begerow et al., 1995; Kozdron-Zabiegala et al., 1995; Baldan et al., 1999; Zabiegala et al., 2002).

Radial diffusive samplers Radiello models were used (Fig. 1). The diffusive surface is a synthesized polyethylene cylinder. The adsorbent was activated charcoal (530 mg). The adsorbed compounds were analysed by gas chromatography (GC/FID, GC/MS) after a CS₂ extraction (Cocheo et al., 1996). The gas chromatographic column was a DB1 (Alltech; 60 m, 0.32 mm and 0.25 μm). An internal standard 2-fluorotoluene was used for quantitative analysis (Meybeck et al., 2000).

The average concentration (C , μg/m³) relative to the sampling period is given by the following expression: $C = m \cdot 10^6 / (Q \cdot t)$, where m (μg) is the mass collected over a period t (minutes) and Q (cm³/min) is the uptake rate (evaluated from laboratory experiments).

Blank values were determined on preconditioned tubes which were carried with sample tubes during the sampling process. Sampling capacity and extraction efficiency of the tubes as well as stability of the compounds in the tubes were tested in earlier studies (Meybeck et al., 2000). Repeatability for benzene, toluene and xylenes was very good. The standard deviation of triplicate samples collected at same sites during both campaigns was below 10% for all compounds.

2.2. Geographical zone and site selection

Toulouse is the fifth urban area in France with 351 822 inhabitants (INSEE census, 1999). The study area affects around 380 000 inhabitants.

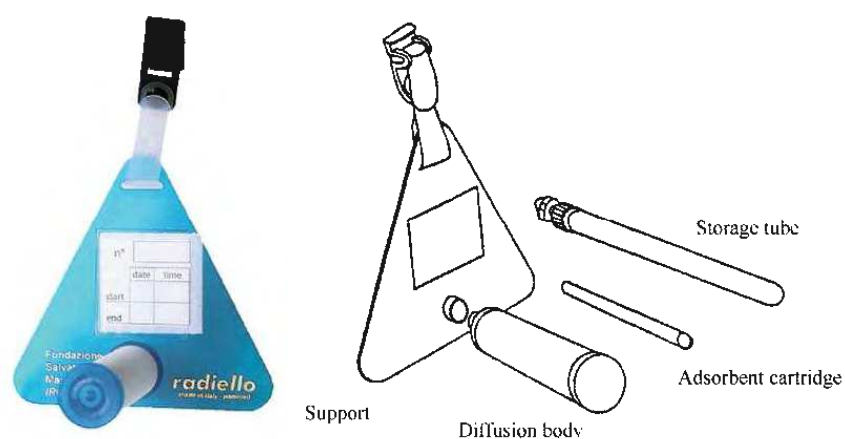


Fig. 1. Radiello diffusive sampler.

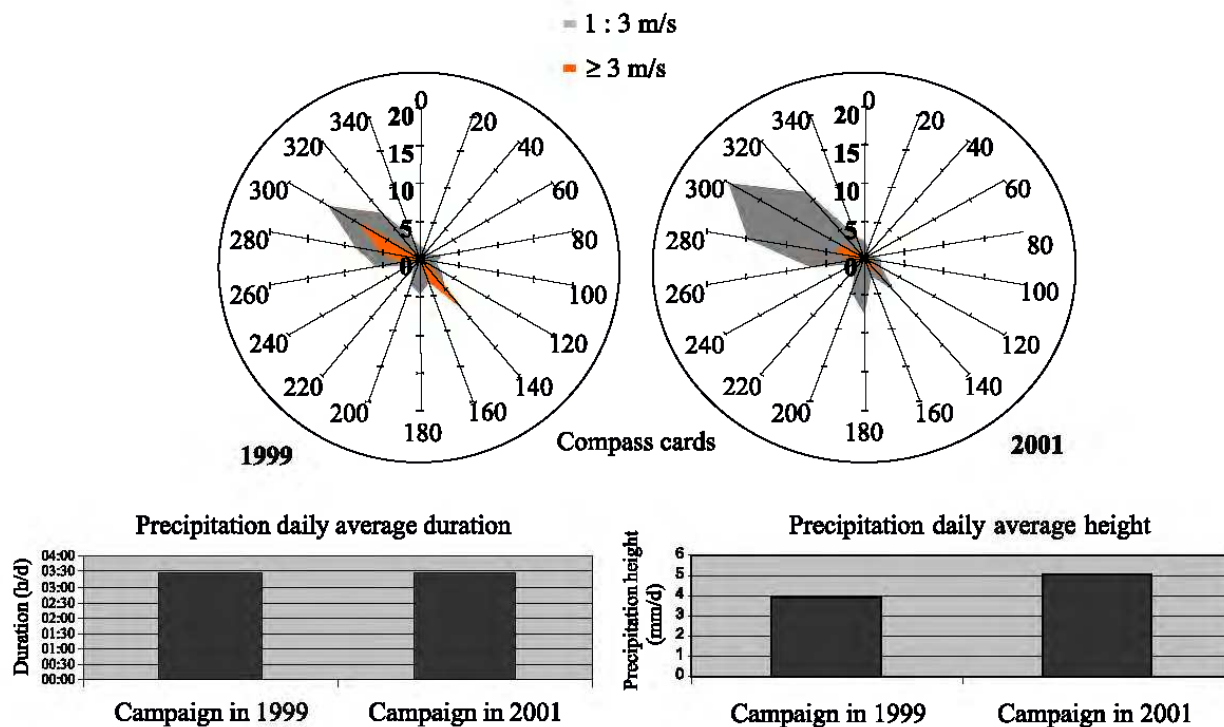


Fig. 2. Meteorological conditions for both global campaigns: 1999 (left; May 5th to 26th and June 14th to July 2nd) and 2001 (right; May 2nd to 22nd and June 13th to July 4th).

We have selected about 60 sites spread over an area of about 250 km². They were chosen among those previously used in 1991/92 and 1996/97 NO₂ measurement campaigns (ORAMIP, 1997). The number

of selected sites is a good compromise between the cost of the study and the time available for collecting and analysing a representative data set. Sampling points were arranged over a regular grid of the urban

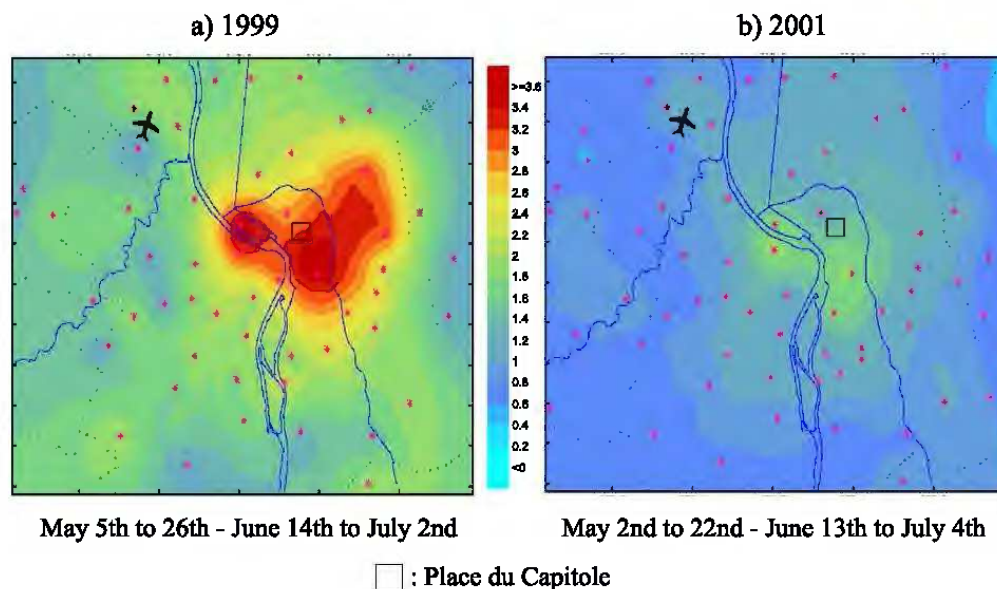


Fig. 3. Isoconcentration plots for benzene for both global campaign. (a) 1999; (b) 2001.

Table 1

Average concentration in BTX over Toulouse in 1999 (May 5th to 26th and June 14th to July 2nd)

| ($\mu\text{g}/\text{m}^3$) | Benzene | Toluene | <i>m,p</i> -Xylene | <i>o</i> -Xylene | All xylenes | All BTX |
|------------------------------|---------|---------|--------------------|------------------|-------------|---------|
| Average concentration | 2.0 | 6.6 | 3.7 | 1.2 | 4.9 | 11.0 |
| Standard deviation | 0.7 | 2.5 | 1.5 | 0.5 | 1.9 | 4.1 |
| Maximum value | 3.8 | 14.1 | 8.0 | 2.7 | 10.6 | 23.1 |
| Minimum value | 1.1 | 3.0 | 1.6 | 0.6 | 2.2 | 5.1 |

area and were taken sufficiently far away from pollution sources to be representative of the background pollution level. The dosimeters were thus generally installed on poles, at 2-m high, in such a way to avoid any wall-screening effect. They were placed in polyethylene boxes in order to ensure protection against rain and solar radiation and to minimize disturbances due to the wind velocity.

2.3. Isoconcentration plots

Cartographic representations were made with the geostatistic computer program ISATIS which provides a set of statistical tools for incorporating the spatial coordinates of observations in data processing, allowing for description and modelling of spatial patterns, prediction at unsampled locations and assessment of the associated uncertainty.

We provide here representative plots corresponding to benzene, toluene and xylenes for both global campaigns.

3. Results and discussion

3.1. Meteorological conditions

Fig. 2 summarizes the mean meteorological conditions for both years. Precipitations did not allow a more important atmosphere washing for one or another campaign. For both periods, main wind directions followed a northwest to southeast line: it is the usual wind configuration in Toulouse. The 1999 period was marked by a wind speed more important.

3.2. BTX concentrations in 1999

Atmospheric average concentrations in benzene reach maximum values of $3.8 \mu\text{g}/\text{m}^3$ in the town center (Fig. 3a), whereas toluene and xylenes are characterized by maximum concentrations being respectively of the order of 14 and $11 \mu\text{g}/\text{m}^3$ (Table 1; Figs. 4a and 5a), corresponding to a maximum concentration in BTX at a given site of about $23 \mu\text{g}/\text{m}^3$.

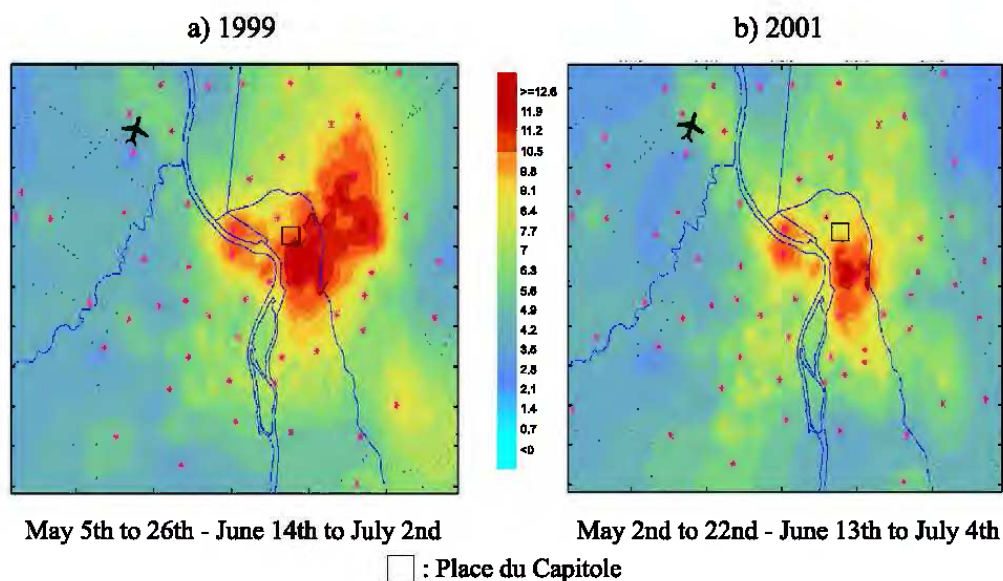


Fig. 4. Isoconcentration plots for toluene for both global campaign. (a) 1999; (b) 2001.

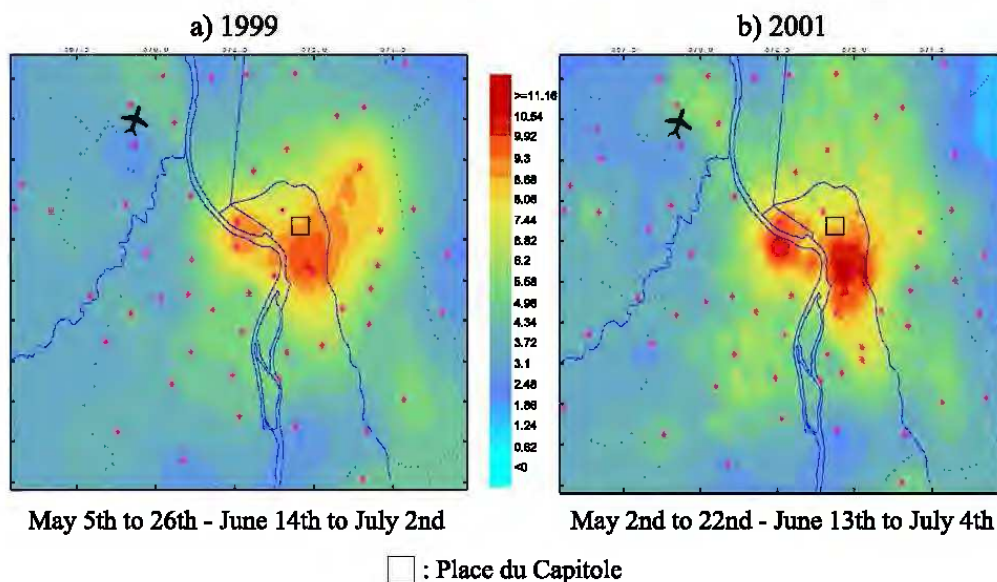


Fig. 5. Isoconcentration plots for xylenes for both global campaign. (a) 1999; (b) 2001.

Let us note that the benzene concentrations recorded here are only representative of the sampling period of the experiment and remain slightly below the upper tolerated value of $5 \mu\text{g}/\text{m}^3$ imposed by the European regulation project.

It is noteworthy that the concentrations reach a maximum within the downtown center and are seen to decrease progressively toward the periphery. The zones exhibiting the highest concentrations are shifted towards the east, which can be understood because of the prevailing eastbound wind effectively recorded during the sampling period.

An evaluation of toluene/benzene and xylene/benzene concentration ratios is useful for characterizing the distance of vehicular emission sources (Derwent et al., 2000). Here, the average recorded concentrations led to toluene/benzene ratios close to 3 (ranged between 2.9 and 3.7), whereas the *m,p*-xylenes/benzene and *o*-xylene/benzene ratios were respectively of the order of 2 and 0.7 (Table 2). These ratios are of the same magnitude as those obtained from automotive exhausts, thereby confirming an origin of the pollution by BTX over Toulouse. In addition, the minimum toluene/benzene concentration ratios are observed on remote sites of the urban area, whereas the maximum ones are detected close to areas where an intense traffic exists. This is in agreement with an earlier observation by Gelencser et al. (1997) that the tolu-

ene/benzene ratio decreases as the distance from the pollution source increases.

3.3. BTX concentrations in 2001. Comparison

Atmospheric concentrations in benzene reach maximum values of $2 \mu\text{g}/\text{m}^3$ in the town center (Fig. 3b), whereas toluene and xylenes are characterized by maximum concentrations being respectively of the order of 11.9 and $11 \mu\text{g}/\text{m}^3$ (Table 3; Figs. 4b, 5b), corresponding to a maximum concentration in BTX at a given site of about $20 \mu\text{g}/\text{m}^3$.

For both campaigns, VOC concentrations are maximum in downtown Toulouse and decrease progressively toward the periphery. The highest concentration zones seem to follow a northwest to southeast line corresponding to wind axis. The wind speed more

Table 2
Ratio between toluene/benzene, *m,p*-xylene/benzene, *o*-xylene/benzene concentrations in 1999

| | Campaign 1999 | Automotive exhaust |
|----------------------------|---------------|--|
| Toluene/benzene | 3.3 | 2.7 (Brocco et al., 1997; Guicherit, 1997) |
| <i>m,p</i> -Xylene/benzene | 1.9 | 1.8 (Stevenson et al., 1997) |
| <i>o</i> -Xylene/Benzene | 0.7 | 0.9 (Guicherit, 1997) |

Table 3

Average concentration in BTX over Toulouse in 2001 (May 2nd to 22nd and June 13th to July 4th)

| ($\mu\text{g}/\text{m}^3$) | Benzene | Toluene | <i>m,p</i> -Xylene | <i>o</i> -Xylene | All xylenes | All BTX |
|------------------------------|---------|---------|--------------------|------------------|-------------|---------|
| Average concentration | 1.1 | 6.1 | 4.0 | 1.3 | 5.3 | 10.0 |
| Standard deviation | 0.3 | 2.1 | 1.5 | 0.5 | 2.0 | 3.4 |
| Maximum value | 2.0 | 11.9 | 8.4 | 2.7 | 11.0 | 19.7 |
| Minimum value | 0.7 | 3.0 | 1.6 | 0.6 | 2.1 | 5.0 |

important in 1999 does not seem to have favoured a better pollutant dispersion.

The average concentrations in BTX over Toulouse corresponding to the two campaigns are displayed in Table 3.

For the 2001 period, benzene average concentrations have been divided by two compared to 1999, whereas toluene and xylene concentrations are statistically the same. Meteorological conditions are almost identical. Thus, for the 2001 study period, the benzene allowable rate decrease from 5% to 1% in gasoline has had a significant effect on benzene concentrations in ambient air in Toulouse. Such decrease of ambient benzene concentrations have also been observed between 1999 and 2000 in Paris (AIRPARIF network), around 42% (<http://www.airparif.asso.fr>).

For the 1999 period, benzene concentrations in most of the study area exceeded $2 \mu\text{g}/\text{m}^3$ (French quality focus) but they remained below $5 \mu\text{g}/\text{m}^3$ (European limit value), whereas for the 2001 period, benzene concentrations were within the French quality value in the whole area. However, those regimentations are given for a whole year. Accordingly, it will be important to measure benzene over annual periods in order to know its concentration over such a period and to observe its seasonal variations.

4. Conclusion

BTX, pollutants directly resulting from automotive exhausts and also from evaporative emissions, are notably toxic to human health and can also generate secondary pollutants like ozone, aldehydes and acids whose impact can be at least as deleterious toward man, ecosystems, monuments. . .

In this context, our goal was to evaluate average atmospheric background concentrations in BTX over

the urban area of Toulouse over a period of several weeks.

We were led to adopt a passive sampling technique which appeared particularly appropriate for that purpose. About 60 sites were selected among the most representative of the Toulouse urban area. A mapping of concentrations reveals that maximum concentrations in BTX are recorded in the downtown area, with a progressive decrease toward the periphery. The areas exhibiting the maximum pollution level are slightly shifted toward east relative to the town center as a consequence of prevailing eastbound winds recorded during the time of the experiment.

Upon consideration of toluene/benzene and xylene/benzene ratios, we conclude that BTX pollution over Toulouse is in particular linked to the motor vehicle exhaust gases.

Benzene average concentrations have been divided by two in 2001 compared to 1999, whereas toluene and xylene concentrations are approximately the same. For the 2001 study period, the benzene allowable rate decrease from 5% to 1% in gasoline has had a significant effect on benzene concentrations in ambient air in Toulouse.

The benzene average amount in 2001 remain below $2 \mu\text{g}/\text{m}^3$, the French quality standard and well under the average value of $5 \mu\text{g}/\text{m}^3$, to which is tending European regulation, knowing that those regimentations are fixed for a whole year. Accordingly, it will be important to measure benzene over annual periods in order to know its exact amount over such a period and to observe its potential seasonal variations.

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